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COMPOSITION CONTAINING INORGANIC LAYERED COMPOUND  
[Muki soyo kagobutsu gan'yu soseibutsu]

Setsu Okino, et al.

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INVENTOR	(72):	SUMITOMO CHEMICAL CO., LTD.
APPLICANT	(71):	OKINO, SETSU; KURODA, TOSHIYA, SAKATANI, TAIICHI
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[Claim 1] A composition containing an inorganic layered compound, characterized by using a high-pressure dispersion apparatus to treat a saponified ethylene-vinyl ester copolymer, an inorganic layered compound, and a solution containing water at a ratio by weight of at least 1/10 water.

[Claim 2] The composition containing an inorganic layered compound according to Claim 1, characterized by the inorganic layered compound and the saponified ethylene-vinyl ester copolymer having a composition ratio by volume of 10/1 to 1/100 (inorganic layered compound/saponified ethylene-vinyl ester copolymer).

[Claim 3] The composition containing inorganic layered compound according to Claim 1 or 2, wherein the inorganic layered compound has an aspect ratio of 50 to 5000.

[Claim 4] The composition containing an inorganic layered compound according to any one of Claims 1 to 3, characterized by the inorganic layered compound having a particle size of 1  $\mu\text{m}$  or less.

[Claim 5] The composition containing inorganic layered compound according to any one of Claims 1 to 4, characterized by the high-pressure dispersion apparatus dispersing under pressure conditions of at least 100  $\text{kgf/cm}^2$ .

[Claim 6] A resin composition containing an inorganic layered compound, characterized by using a high-pressure dispersion apparatus

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\* Claim and paragraph numbers correspond to those in the foreign text.

to treat a saponified ethylene-vinyl ester copolymer, an inorganic layered compound, and a solution containing water at a ratio by weight of at least 1/10, then eliminating the solvent.

[Claim 7] A composition containing the composition containing an inorganic layered compound according to any one of Claims 1 to 5 and another resin.

[Claim 8] A resin composition containing the resin composition containing an inorganic layered compound according to Claim 6, and another resin.

[Claim 9] The composition containing an inorganic layered compound according to any one of Claims 1 to 5, characterized by having no more than 30 cc/m<sup>2</sup>-day-atm oxygen permeation at 23°C and 95% RH (relative humidity) per 1 μm thickness of the resulting film after eliminating the solvent.

[Claim 10] The resin composition containing an inorganic layered compound according to Claim 6, characterized by having no more than 30 cc/m<sup>2</sup>-day-atm oxygen permeation at 23°C and 95% RH (relative humidity) per 1 μm thickness of the resulting film.

[Claim 11] A laminate obtained by coating and drying the composition containing an inorganic layered compound according to any one of Claims 1 to 5 on a substrate.

[Claim 12] A laminate wherein at least one layer is a layer comprising the resin composition containing an inorganic layered compound according to Claim 6.

[Claim 13] A laminate obtained by coating and drying the composition according to Claim 7 on a substrate.

[Claim 14] A laminate wherein at least one layer is a layer comprising the resin composition according to Claim 8.

[Claim 15] A molding comprising the resin composition containing an inorganic layered compound according to Claim 6.

[Claim 16] The molding of Claim 15, wherein the molding is a film.

[Claim 17] The laminate according to any one of Claims 11 to 14, used for a packaging application.

[Claim 18] The molding according to Claim 15 or 16, used for a packaging application.

[Claim 19] The laminate according to any one of Claims 11 to 14, used in a liquid crystal display device.

[Claim 20] The molding according to Claim 15 or 16, used in a liquid crystal display device.

[Claim 21] The laminate according to any one of Claims 11 to 14, used for a facility landscaping application.

[Claim 22] The laminate according to Claim 15 or 16, used for a facility landscaping application.

[DETAILED EXPLANATION OF THE INVENTION]

[0001] [INDUSTRIAL FIELD OF APPLICATION]

The present invention relates to a composition containing an inorganic layered compound.

[0002] [PRIOR ART]

Saponified ethylene-vinyl ester copolymers (hereafter sometimes abbreviated EVOH) have previously come to be used, for example, in packaging material applications for the high gas barrier property in their resin. Japanese Kokai Patent Publications H6-57066A, H1-308627A, and H5-39392A, for example, have reported compositions compounded of EVOH and an inorganic powder for the purpose of improving the gas barrier property even more.

[0003] [PROBLEMS THAT THE INVENTION IS TO SOLVE]

Conventionally, however, a composition compounded of EVOH and an inorganic powder obtained by kneading in a mixer or an extruder, for example, does not give enough gas barrier property to the resulting composition because not enough inorganic powder has been dispersed in the EVOH, and increasing the mixture ratio of the inorganic powder to improve the gas barrier property has had the problem of increasing melt viscosity when kneading. The method of charging and kneading an EVOH solution and an aqueous solution of an inorganic powder also cannot be said to give a composition with good dispersion of the inorganic powder, and the resulting film, for example, has not had satisfactory gas barrier property.

[0004] The object of the present invention is to solve these problems by providing a composition containing EVOH and an inorganic layered compound that stays well dispersed and has excellent stability.

[0005] [MEANS OF SOLVING THE PROBLEMS]

The present inventors achieved the present invention as a result of extensive study toward solving these problems. Specifically, the present invention provides a composition containing an inorganic layered compound characterized by using a high-pressure dispersion apparatus to treat a saponified ethylene-vinyl ester copolymer, an inorganic layered compound, and a solution containing water at a ratio by weight of at least 1/10.

[0006] [EMBODIMENT OF THE PRESENT INVENTION]

Next, the present invention will be discussed in detail. The saponified ethylene-vinyl ester copolymer used in the present invention is an ethylene-vinyl ester copolymer that has been saponified. Examples of a vinyl ester are vinyl acetate and vinyl trifluoroacetate. The percentage of ethylene units per units of all monomers is 20% to 60%, preferably 20% to 45%, and more preferably 25% to 40% from the standpoint of the gas barrier property of the resulting composition. The degree of saponification of the vinyl ester units is at least 90%, preferably at least 95%, and more preferably at least 98%. This "degree of saponification of vinyl ester units" refers to the percentage of saponified vinyl ester units out of the total number of vinyl ester units and saponified vinyl ester units present in EVOH. More specific examples are the commercial products EVAL (Kuraray Co., Ltd.) and SOANOL (Nippon Synthetic Chemical Industry Co., Ltd.).

[0007] The EVOH in the present invention can also be a so-called EVOH derivative having a functional group other than hydroxyl. Examples of functional groups other than hydroxyl are amino, thiol, carboxyl, sulfone, phosphoric acid, carboxylate, sulfonate ions, phosphate ions, ammonium, phosphonium, silyl, siloxane, alkyl, allyl, fluoroalkyl, alkoxy, carbonyl, and halogens. Some or all of the hydroxyls in EVOH may be substituted by one or more of these functional groups.

[0008] The "inorganic layered compound" used in the present invention is a compound or a substance having a layered structure of unit crystal layers layered together. "Layered structure" here refers to a structure in which faces tightly arrayed by strongly bonding molecules through covalent bonding, for example, are layered nearly parallel by a weak bonding force such as a Van Der Waals force.

[0009] Specific examples of inorganic layered compounds are graphite, phosphate ion derivative compounds (such as zirconium phosphate compounds), chalcogen compounds, hydrotalcite compounds, lithium-aluminum complex hydroxides, and clay minerals. "Chalcogen compounds" here refers to dichalcogens of a IV Group (Ti, Zr, or Hf), a V Group (V, Nb, or Ta) and/or a VI Group (Mo, or W) element expressed by the formula  $MX_2$  (where M indicates the above elements, and X indicates a chalcogen (S, Se, or Te)). From the standpoint of dispersion, an inorganic layered compound with a property of swelling/cleaving to a solvent such as discussed below is preferred,



and a clay mineral with the property of swelling/cleaving to a solvent is optimal.

[0010] The degree of "swelling/cleaving" property of an inorganic layered compound to a solvent can be assessed by the following "swelling/cleaving" test. The swelling property of the inorganic layered compound is preferably a level of at least about 5 (more preferably at least about 20) in the following swelling test. The cleaving property of the inorganic layered compound is preferably a level of at least about 5 (more preferably at least about 20) in the following cleaving test. The solvent used in these tests is a solvent that has lower density than the inorganic layered compound. If the inorganic layered compound is a naturally swelling clay mineral, the solvent used is preferably water.

[0011] <Swelling Test>

2 g of the inorganic layered compound are slowly combined with 100 mL of the solvent (in a 100 mL measuring cylinder as the vessel). After allowing to rest, the volume of the inorganic layered compound dispersion layer after 24 hours at 23°C is read from the gradation of the interface of this layer (the inorganic layered compound layer) with the supernatant layer. A greater volume indicates a higher swelling property.

[0012] <Cleaving Test>

30 g of the inorganic layered compound are slowly combined with 1500 mL of the solvent. After dispersing in a dispersing machine

(Desper-MH-L made by Asada Iron Works Co., Ltd., blade diameter: 52 mm, rotating speed: 3100 rpm, capacity: 3 L, gap between floor and blades: 28 mm) at a circumferential speed of 8.5 m/sec for 90 minutes (23°C), 100 mL of the dispersion are taken and placed in a measuring cylinder. After allowing to rest for 60 minutes, the volume of the inorganic layered compound dispersion layer is read from the interface of the layer with the supernatant layer.

[0013] Clay minerals are usually classified as a two-layer type having an octagonal layer with a central metal such as aluminum or magnesium above a tetragonal layer of silica, and a type with a three-layer type having two tetragonal layers of silica on both sides of an octagonal layer with a central metal such as aluminum or magnesium. Examples of the former two-layer type are kaolinite and antigorite clay minerals, and examples of the latter three-layer type are smectite, vermiculite, and mica clay minerals depending on the number of interlayer cations.

[0014] More specific examples of these clay minerals are kaolinite, dickite, nacrite, halloysite, antigorite, chrysotile, pyrophyllite, montmorillonite, hectorite, tetrasilylic mica, sodium teniolite, mica, margarite, talc, vermiculite, phlogopite, xanthophyllite, and chlorite. More information can be found in literature such as Haruo Shiromizu, *Clay Mineral Studies*, 1988, Asakura Shoten.

[0015] The solvent used in the present invention contains water

at a ratio by weight of at least 1/10. Examples of solvents other than water are alcohols such as methanol, ethanol, 2-propanol, 1-butanol, pentanol, octanol, or 1,3-pentanediol, ketones such as acetone or methyl ethyl ketone, esters such as methyl acetate or ethyl acetate, and ethers such as n-butyl Cellosolve or ethyl Cellosolve. These solvents may be used alone or mixed. If a composition containing an inorganic layered compound obtained uses a content of water less than 1/10 ratio by weight, the inorganic layered compound in the composition does not have enough stability and is prone to problems such as sediment.

[0016] A solvent mixture of water and an alcohol is preferred from the standpoint of EVOH solubility. Examples of preferred alcohols are methanol, ethanol, 2-propanol, 1-propanol, and 1-butanol. The ratio of water/alcohol in a water/alcohol solvent mixture is preferably 2/8 to 8/2. The alcohol may be one or more types.

[0017] When using the resulting composition containing an inorganic layered compound comprising EVOH and an inorganic layered compound as a coating solution, for example, this solvent is preferably a liquid near room temperature and easily evaporates when this composition is dried. Such a solvent preferably has a boiling point no higher than 200°C (more preferably no higher than 140°C).

[0018] When mixing EVOH and an inorganic layered compound, the inorganic layered compound is preferably added to an EVOH solution,

which is preferably heated before stirring to improve dispersion. The boiling point of the solvent is preferably at least 50°C (more preferably at least 80°C). From the standpoint of this boiling point and the melting point, the solvent is optimally a solvent such as water, methanol, ethanol, 1-butanol, 2-propanol, or 1-propanol. EVOH may be used, for example, as an EVOH dispersion in the form of an emulsion, where the dispersing solvent of the EVOH dispersion is preferably a water/alcohol solvent mixture.

[0019] The composition containing an inorganic layered compound of the present invention can give a composition with better dispersion of the inorganic layered compound by using a high-pressure dispersion apparatus to treat a solution containing EVOH, an inorganic layered compound, and water at a ratio by weight of at least 1/10. When treating in a high-pressure dispersion apparatus, EVOH and the inorganic layered compound may be treated separately before mixing, or both may be mixed before treating. At least one of EVOH and the inorganic layered compound is treated together with a solvent containing at least 1/10 of water. For example, there is a method of treating dispersions containing an EVOH solution and an inorganic layered compound separately in a high-pressure dispersion apparatus, then mixing, a method of mixing EVOH, an inorganic layered compound, and a solvent before treating, and a method of treating a dispersion containing an inorganic layered compound, then mixing this with EVOH before again treating in the high-pressure dispersion

apparatus. In the method of treating EVOH and an inorganic layered compound separately in a high-pressure dispersion apparatus, then mixing, however, the solvent after mixing preferably contains at least 1/10 of water from the standpoint of the stability of the inorganic layered compound after mixing.

[0020] Any sort of operation may be applied to the EVOH, the inorganic layered compound, or a composition of these before or after treating in a high-pressure dispersion apparatus. Examples of such operations are mixing, separating, stirring, dissolving, dispersing, heating, cooling, drying, defoaming, extruding, and allowing to rest. One example is to dissolve EVOH in a solution, disperse the inorganic layered compound in water, and treat a mixture of these in a high-pressure dispersion apparatus to give a composition containing an inorganic layered compound, then combine the resulting liquid composition with a surfactant, for example, and stir. The resulting composition can be optimally used as a coating solution, as will be discussed later.

[0021] The mixing method is not specifically limited when mixing the inorganic layered compound with EVOH before treating in a high-pressure dispersion apparatus. For example, when using EVOH as an EVOH solution, any of several methods may be used, such as the method of first dissolving EVOH in a water/alcohol solvent mixture containing at least 1/10 of water, then combining with an inorganic layered compound and dispersing, and the method of mixing a

dispersion of an inorganic layered compound and an EVOH solution.

[0022] The vessel used for mixing preferably has, for example, a jacket on the outer wall capable of passing a heat medium such as hot water or steam for temperature control. From the standpoint of capturing bubbles and forming an even dispersion, a structure with a baffle or the like is preferably used inside the vessel. The position of the dispersing blades is preferably offset somewhat from the center of the kiln for the same reasons. For a higher concentration of solid parts and better dispersion, the method of stirring at a high speed of 4000 to 7000 rpm inside a kiln lowered to a pressure no higher than 200 mmHg so as not to capture bubbles facilitates obtaining a high shearing power effect.

[0023] The "high-pressure dispersion apparatus" in the present invention is an apparatus for creating, for example, a high shearing or high pressure state under specific conditions by passing a composition mixing particles to be dispersed with a solvent or the like through a plurality of small tubes and impacting at high speed. For example, passing a composition through small tubes of 1 to 1000  $\mu\text{m}$  diameter is preferred, and the maximum pressure condition on this composition is preferably a pressure of at least 100  $\text{kgf/cm}^2$ , and preferably at least 500  $\text{kgf/cm}^2$ . The maximum speed reached by a composition when passing the composition through a high-pressure dispersion apparatus is preferably at least 100 m/sec, and the rate of heat transfer is preferably at least 100 kcal/hr.

[0024] Fig. 1 schematically shows the principles of a high-pressure treatment section in a high-pressure dispersion apparatus used in the present invention. In Fig. 1, the pump (B) applies a high pressure on a treatment sample in the portion of the small tubes (C) and (D). If the flow speed at the location instantaneously reaching the maximum speed is 300 m/sec, for example, the sample passes through the center of a cube with a volume of  $1 \times 10^{-3} \text{ m}^3$ , and pressure loss when the sample temperature rises to 35°C transmits energy to the sample. If the specific gravity of the sample is 1 g/cm<sub>3</sub> and the specific heat is 1 cal/g°C, the rate of heat transfer is  $3.8 \times 10^4$  kcal/h.

[0025] An example of such a high-pressure dispersion apparatus is an Ultrahigh-Pressure Homogenizer made by Microfluidics Corporation (trade name: Microfluidizer) or a Nanomizer made by Nanomizer Co. Another example is a Manton-Gaulin high pressure dispersing apparatus or a homogenizer made by Izumi Food Machinery. When using a Microfluidizer as a high-pressure dispersion apparatus, an EVOH solution of EVOH dissolved in a solvent is preferably used to keep the treatment sample fluid at the temperature used for treatment.

[0026] When using the composition containing an inorganic layered compound of the present invention by coating, as high a total concentration of solid parts as possible is preferred from the standpoint of drying after coating, and both EVOH and the inorganic

layered compound are preferably as high a concentration as possible.

[0027] Although not specifically limited, the composition ratio (by volume) of the inorganic layered compound to EVOH is a ratio by volume of inorganic layered compound/EVOH (ratio when "charged") of usually 10/1 to 1/100 and preferably at least 5/95 from the standpoint of gas barrier property, and no higher than 90/10 from the standpoint of formability. From the standpoint of the softness of the resulting molding, the ratio by volume is preferably 5/95 to 30/70, and optimally 10/90 to 30/70. When used as a film or a laminate, the ratio by volume is preferably at least 7/93 from the standpoint of minimizing reduction in physical properties by bending, and preferably no higher than 17/83 from the standpoint of softness and minimizing peeling from the substrate.

[0028] This ratio by volume can be found by dividing the numerator (the weight of the inorganic layered compound) by the denominator (the weight of EVOH) expressed as ratios by weight when these ingredients are "charged" by the density of these ingredients.

[0029] Various solvents may be added to the composition containing an inorganic layered compound of the present invention for purposes such as improving coating or adjusting viscosity, and additives can be added as required. Examples of additives are pigments, surfactants, fungicides, preservatives, crosslinking agents, antifoaming agents, and antioxidants.

[0030] Examples of pigments are primer antirust pigments,



coloring pigments, metallic foil pigments, bright pigments, and volume pigments. Examples of primer antirust pigments are strontium chromate, zinc chromate, zinc phosphate, red lead, zinc white, basic sulfate, and basic carbonate. Examples of coloring pigments are phthalocyanine blue, phthalocyanine green, quinacridone, indanthrone, isoindolinone, perylene, anthrapyrimidine, benzimidazolone, carbon black, titanium dioxide, graphite, yellow iron oxide, and red iron oxide.

[0031] Examples of metallic foil pigments are aluminum foil, bronze foil, tin foil, gold foil, silver foil, copper foil, metallic titanium foil, stainless steel foil, nickel foil, chromium foil, and foils of alloys of these metals and metallic foils coated with plastics.

[0032] Examples of bright pigments are mica foil and phthalocyanine blue in the form of a foil. Examples of volume pigments are calcium carbonate, gypsum, clay, and talc.

[0033] Examples of surfactants are any nonionic, anionic, cationic, and amphoteric surfactants suitably selected for use considering the stability of the treatment solution and operability such as defoaming and coating properties.

[0034] Examples of nonionic surfactants are polyoxyethylene glycol, polyoxyethylene polyoxypropylene glycol, polyoxypropylene glycol, polyoxyethylene alkyl phenyl ether, glycerin fatty acid partial ester, sorbitan fatty acid partial ester, pentaerythritol

fatty acid partial ester, polyoxyethylene sorbitan fatty acid partial ester, and polyoxyethylene alkyl ether.

[0035] Examples of anionic surfactants are dialkyl sulfonic amber acid salt, alkyl naphthalene sulfonate, polyoxyethylene alkyl sulfonate, alkyl phosphoric acid ester salt, polyoxyethylene alkyl ether phosphoric acid ester salt, sulfuric acid ester salts of fatty acid alkyl esters, alkyl sulfonic ester salt, polyoxyethylene alkyl ether sulfuric acid ester salt, and fatty acid monoglyceride sulfuric acid ester salt. Examples of cationic surfactants are alkyl amine salts and dialkyl amine salts. An example of an amphoteric surfactant is N,N,N-trialkyl-N-sulfoalkylene ammonium betaine.

[0036] Usable fungicides and preservatives include quaternary ammonium salts, nitrogen-containing sulfur compounds, halogenated sulfur compounds, organic iodine compounds, and benzimidazole compounds. Specific examples of fungicides are 2-thiazol-4-yl benzimidazole, methylbenzimidazol-2-yl carbamate, N-dichlorofluoromethylthio-N',N'-dimethyl-N-phenyl sulfamide, tetramethylthiuram disulfide, N-(trichloromethylthio)-4-cyclohexene-1,2-dicarboxyimide, 2,4,5,6-tetrachloro-1,3-isophthalonitrile, 2,3,5,6-tetrachloro-4-(methylsulfonyl)pyridine, and bis(2-pyridylthio)-zinc-1,1-dioxide. Considering heat resistance, 2-thiazol-4-yl benzimidazole, methylbenzimidazol-2-yl carbamate, 2,4,5,6-tetrachloro-1,3-isophthalonitrile, and bis(2-pyridylthio)-zinc-1,1-dioxide are preferred.

[0037] Specific examples of bactericides are 1,2-benzisothiazolin-3-one (BIT), 2,3,5,6-tetrachloro-4-(methylsulfonyl)pyridine, and 10,10'-oxybisphenoxy arsine.

[0038] Examples of crosslinking agents are titanium couplers, silane couplers, melamine couplers, epoxy couplers, isocyanate couplers, copper compounds, and zirconium compounds. Zirconium compounds are optimally used from the standpoint of improving moisture resistance. Specific examples zirconium compounds are zirconium halides such as zirconium oxychloride, zirconium hydroxychloride, zirconium tetrachloride, or zirconium bromide; zirconium salts of mineral acids, such as zirconium sulfate, basic zirconium sulfate, or zirconium nitrate; organic zirconium salts such as zirconium formate, zirconium acetate, zirconium propionate, zirconium caprylate, or zirconium stearate; and zirconium complex salts such as zirconium ammonium carbonate, zirconium sodium sulfate, zirconium ammonium acetate, zirconium sodium oxalate, or zirconium sodium citrate. Although not specifically limited, the content of a crosslinking agent is preferably a ratio (K) of mols of crosslink producing groups in the crosslinking group (CN) to mols of groups coupling hydrogen in the resin (HN) ( $K = CN/HN$ ) in a range of 0.001 to 10. This molar ratio K is more preferably in a range of 0.01 to 1.

[0039] When using the composition containing an inorganic layered compound of the present invention for coating, a solvent can be added to improve wettability when coating. The solvent used is

preferably a solvent that by itself is a liquid near room temperature, but evaporates when coated and dried on a substrate. Examples of such solvents are alcohols such as methanol, ethanol, 2-propanol, 1-butanol, pentanol, or octanol, and acetone, methyl ethyl ketone, and ethyl acetate. Several types of solvents may be used. The solution prepared in this way can be used by coating, dip coating, or brush coating.

[0040] The following are examples of indices for assessing the dispersion of the inorganic layered compound in the composition containing an inorganic layered compound of the present invention. Examples of methods for a liquid composition dispersed in a solvent are a method of making the composition a thin cast film, for example, on a smooth substrate (for example, a glass plate) and assessing its appearance by comparison (solidified matter can be assessed visually if poorly dispersed), and a method of assessing based on the average particle size of the inorganic layered compound when dispersed in a dispersing medium by itself (R0), by how close the average particle size of the inorganic layered compound when dispersed in an EVOH solution or dispersion (R) is to R0.

[0041] Other potential methods include a method of finding the average particle size of the inorganic layered compound in the composition, a method using diffraction/scattering, a method using dynamic light scattering, a method using change in electrical resistance, and a method using image processing after photographing a

microscopic image. If the composition has essentially little scattering (is transparent) and the scattering is overwhelmingly derived from the inorganic layered compound, the method using diffraction/scattering is more preferred use for obtaining information for just the particle size distribution of the inorganic layered compound regardless of whether a resin is present.

[0042] The particle size distribution and the average particle size are measured in the diffraction/scattering method by using the Mie scattering theory to calculate the particle size distribution that least contradicts the diffraction/scattering pattern obtained when light is passed through the dispersion. Examples of commercial apparatuses are laser diffraction and light scattering particle size analyzers LS230, LS200, and LS100 made by Coulter, laser diffraction particle size distribution analyzers SALD2000, SALD2000A, and SALD3000 made by Shimadzu, laser diffraction and scattering particle size distribution analyzers LA910, LA700, and LA500 made by Horiba, and Microtrack SPA and Microtrack FRA made by Nikkiso.

[0043] The solution is preferably not diluted when measuring particle size distribution. For solutions with too strong scattering and low transparency, shortening the optical path will allow measurement without diluting (for example, in the case of LA910 made by Horiba, the optical path can be significantly shortened using, for example, a patch cell or a paste cell). Dispersion is often unchanged, however, when diluted by a solvent with the same

ingredients as used in the liquid composition, in which case, dispersion may be assessed by measuring the diluted solution.

[0044] This measurement method cannot identify particles separately if the distance between particles is less than the wavelength of the light source, and so recognizes several adjacent particles separated (for example, by a resin in between) by a certain distance (for example, submicron or less) as one particle. Therefore, this method cannot assess cases in which poor dispersion is caused not just by particles cohering, but also by having a resin in between.

[0045] The composition containing an inorganic layered compound used in the present invention preferably has an aspect ratio of 50 to 5000 from the standpoint of gas barrier property. This aspect ratio (Z) is a ratio found by the relation  $Z = L/a$ , where L is the particle size (the median diameter based on volume) of the inorganic layered compound in the dispersion found by measuring the particle size by the diffraction/scattering method discussed earlier, and a is the unit thickness of the inorganic layered compound. This "unit thickness a" is determined based on measuring an inorganic layered compound unit, for example, by powder x-ray diffraction analysis as discussed later. More specifically, as shown schematically by the graph of Fig. 2 plotting  $2\theta$  on the horizontal axis and the intensity of the x-ray diffraction peak on the vertical axis, the spacing found based on Bragg's equation ( $n\lambda = 2D\sin\theta$ ,  $n = 1, 2, 3 \dots$ ) from the angle

$\theta$  corresponding to the peak with the lowest angle of the observed diffraction peaks is taken as "unit thickness  $a$ ." (For details of powder x-ray diffraction analysis, see, for example, Jiro Shiokawa, ed., *Machine Analysis Procedure (a)*, p. 69 (1985), Kagaku Dojinsha.)

[0046] The spacing  $d$  of the inorganic layered compound in a resin composition can usually be found during powder x-ray diffraction of this resin composition after eliminating the solvent from the dispersion. More specifically, as shown schematically by the graph of Fig. 3 plotting  $2\theta$  on the horizontal axis and the intensity of the x-ray diffraction peak on the vertical axis, the spacing corresponding to the peak with the lowest angle of the diffraction peaks observed on the lower angle (larger spacing) side from the position of the diffraction peak corresponding to the "unit thickness  $a$ " discussed earlier is taken as "spacing  $d$ " ( $a < d$ ). As shown schematically in the graph of Fig. 4, if the peak corresponding to this "spacing  $d$ " overlaps a halo (or background), making the peak difficult to detect, the area of the part of the lower angle side from  $2\theta d$  to the baseline is taken as the peak corresponding to "spacing  $d$ ." This " $\theta d$ " is the diffraction angle corresponding to "(unit thickness  $a$ ) + (width of one resin main chain)." (For details of the method for determining spacing  $d$ , see, for example, Shuichi Iwao, ed., *Dictionary of Clays*, pp. 35ff and pp. 271ff, 1985, Asakura Shoten.)

[0047] The "integrated intensity" of a diffraction peak

(corresponding to the spacing  $d$ ) observed during powder x-ray diffraction of a resin composition in this way is preferably at least twice (more preferably at least ten times) the integrated intensity of the diffraction peak taken as the standard (corresponding to the "unit thickness  $a$ "). Usually, the difference between this spacing  $d$  and the "unit thickness  $a$ ", namely  $k = (d - a)$  (converted to "length"), is equal to or greater than the width of one main chain of the resin comprising the resin composition ( $k = (d - a) \geq$  width of one resin main chain). This "width of one resin main chain" can be found, for example, by simulation calculation (see, for example, *Introduction to Polymer Chemistry*, pp. 103-110, 1981, Kagaku Dojin), and is four to five angstroms in the case of polyvinyl alcohol (two to three angstroms in the case of a water molecule).

[0048] This aspect ratio  $Z = L/a$  is suitable for approximating the "true aspect ratio" by this aspect ratio  $Z$  for the following reasons: Although the "true aspect ratio" of an inorganic layered compound in a resin composition is extremely difficult to measure directly. The spacing  $d$  of the resin composition found by powder x-ray diffraction analysis and the "unit thickness  $a$ " found by measuring the powder x-ray diffraction of the inorganic layered compound alone have the relation  $a < d$ . If  $(d - a)$  is at least the width of one main chain of the resin in this resin composition, the resin is inserted between the inorganic layered compound in the resin composition. Therefore, a suitable approximation can be found by



approximating the thickness of the inorganic layered compound in the resin composition by this "unit thickness  $a$ ;" that is, approximating the "true aspect ratio" in the resin composition by the "aspect ratio  $Z$ " of the inorganic layered compound in the dispersion.

[0049] As discussed earlier, it is extremely difficult to measure the true particle size in a resin composition, but the particle size of the inorganic layered compound in the resin can be viewed as fairly close to the particle size of the inorganic layered compound in the dispersion (resin/inorganic layered compound/solvent). Since it appears rather unlikely that the particle size  $L$  in the dispersion found by the diffraction/scattering method would be greater than the long diameter  $L_{\max}$  of the inorganic layered compound, however, the true aspect ratio ( $L_{\max}/a$ ) is theoretically fairly likely to be less than the "aspect ratio  $Z$ " used in the present invention ( $L_{\max}/a < Z$ ).

[0050] These two considerations suggest that the definition  $Z$  of the aspect ratio used in the present invention is a suitable enough approximation. "Aspect ratio" or "particle size" in the present specification refers to the "aspect ratio  $Z$ " or the "particle size  $L$  found by the diffraction/scattering method" defined above.

[0051] The inorganic layered compound used in the present invention preferably has an aspect ratio as defined above of at least 50, more preferably at least 100, still more preferably at least 200, and optimally at least 500 from the standpoint of gas barrier

property. From the standpoint of production, the aspect ratio is preferably no higher than 5000, more preferably no higher than 3000, still more preferably no higher than 2000, and optimally no higher than 1500.

[0052] The inorganic layered compound used in the present invention preferably has a particle size measured by the method discussed earlier of no greater than 5  $\mu\text{m}$  from the standpoint of formability, and no greater than 3  $\mu\text{m}$  from the standpoint of transparency. When used in an application emphasizing transparency (for example, for packaging foods), this particle size is optimally no greater than 2  $\mu\text{m}$ .

[0053] Other resins besides EVOH may be added to the composition containing an inorganic layered compound of the present invention. Examples of other resins are polyolefin resins such as polyethylene (low density or medium density), ethylene-propylene copolymer, ethylene-butene copolymer, ethylene-hexene copolymer, ethylene-octene copolymer, polypropylene, ethylene-vinyl acetate copolymer, ethylene-methyl methacrylate copolymer, or ionomer resins.

[0054] The composition containing an inorganic layered compound of the present invention obtained as discussed earlier can be made a resin composition containing an inorganic layered compound by eliminating the solvent by means such as drying. The resulting resin composition containing an inorganic layered compound may be mixed with the same resins other than EVOH. Examples of mixing methods are

any standard methods used to mix resins.

[0055] The composition containing an inorganic layered compound of the present invention can be made a molding by means such as cast film formation, and can be made a laminate by coating and drying on a substrate such as discussed later. Examples of laminate production methods are methods such as the method of making a composition containing an inorganic layered compound a substrate a dried film (by a method such as cast film formation), then pasting on a substrate, and the method of coating and drying a composition on a substrate. The latter method is especially preferred.

[0056] Examples of coating methods are roll coating methods such as direct gravure, reverse gravure, micro gravure, double roll beat coating, or bottom feed triple reverse coating, and doctor knife coating, die coating, dip coating, bar coating, and combinations of these coating methods.

[0057] The thickness of the layer formed from the composition containing an inorganic layered compound when making a laminate is a thickness when dry of preferably 30  $\mu\text{m}$  or less and more preferably 10  $\mu\text{m}$  or less, depending on the desired properties of the laminate. A thickness of 1  $\mu\text{m}$  or less has the advantage of giving the layer formed from the composition high transparency, which is more preferred for applications of the present invention requiring transparency. Although the lower limit is not specifically limited, the thickness is preferably at least 1 nm, more preferably at least

10 nm, and optimally at least 100 nm to obtain the desired effects.

[0058] The substrate is not specifically limited, and may be any of a film, a sheet, a bottle, or a tray, for example, without limitation. The material of the substrate can be any conventional and generally used material, such as resin, paper, aluminum foil, wood, fabric, or synthetic fabric, depending on the purpose and application. If a film, besides undrawn film, the film may be uniaxially or biaxially drawn. Needless to say, the film may be subjected to a conventional treatment such as undercoating or corona treatment. These surface treatments may be applied not just to film, but other substrate modes within a range that does not hinder the object of the present invention.

[0059] Examples of the resin comprising the substrate are polyolefin resins such as polyethylene (low density or high density), ethylene-propylene copolymer ethylene-butene copolymer, ethylene-hexene copolymer, ethylene-octene copolymer polypropylene, ethylene-vinyl acetate copolymer, ethylene-methyl methacrylate copolymer, or ionomer resins; polyester resins such as polyethylene terephthalate (PET), polybutylene terephthalate, or polyethylene naphthalate; amide resins such as Nylon-6, Nylon-6,6, metaxylene diamine-adipic acid condensate, or polymethyl methacrylamide; acrylic resins such as polymethyl methacrylate; styrene and acrylonitrile resins such as polystyrene, styrene-acrylonitrile copolymer styrene-acrylonitrile-butadiene copolymer, or polyacrylonitrile; hydrophobic cellulose

resins such as cellulose triacetate or cellulose diacetate; halogenated resins such as polyvinyl chloride, polyvinylidene chloride, polyvinylidene fluoride, or polytetrafluoroethylene (Teflon); hydrogen-bonded resins such as polyvinyl alcohol, ethylene-vinyl alcohol copolymer or cellulose derivatives; and polycarbonate resins, polysulfonated resins, polyether sulfone resins, polyether ether ketone resins, polyphenylene oxide resins, polymethylene oxide resins, and engineering plastics such as liquid crystal resins.

[0060] As noted earlier, the resin composition containing an inorganic layered compound can also be formed by a conventional method as a molding such as a film, or can be laminated by a conventional method such as coextrusion on a substrate such as discussed earlier to form a laminate.

[0061] If the substrate is transparent, the composition containing an inorganic layered compound and the resin composition containing an inorganic layered compound are preferably transparent. This transparency is preferably a transparency to all light of 500 nm wavelength of about at least 80% (more preferably at least 85%, and optimally at least 90%). Such a transparency can be advantageously measured, for example, by a self-recording spectrophotometer model 330 made by Hitachi, Ltd. Haze is preferably 25% or less, more preferably 20% or less, and optimally 15% or less, and may be measured using a commercial Haze Meter (made by Suga Test Instruments).

[0062] Laminates obtained by forming or laminating the composition containing an inorganic layered compound and the resin composition containing an inorganic layered compound of the present invention may be used in a variety of applications. Examples of such applications are a phase difference film utilizing its double refraction, a gas-low molecular weight diffusion barrier film or molding utilizing the low molecular weight diffusion delaying effect of its layered structure, and facility landscaping applications during construction such as greenhouses or tunnels. When used as a gas barrier film in food and pharmaceutical packaging, the composition can be used as a molding by printing or laminating another film on this film.

[0063] From the standpoint of gas barrier property, 1  $\mu\text{m}$  thickness of a film obtained by eliminating the solvent from the composition containing an inorganic layered compound and a film comprising the resin composition containing an inorganic layered compound of the present invention has an oxygen permeation at 23°C and 50% RH of preferably 30  $\text{cc}/\text{m}^2\text{-day-atm}$ , more preferably 5  $\text{cc}/\text{m}^2\text{-day-atm}$ , and still more preferably 1  $\text{cc}/\text{m}^2\text{-day-atm}$ . For applications requiring greater gas barrier property, this oxygen permeation is preferably 0.1  $\text{cc}/\text{m}^2\text{-day-atm}$ , more preferably 0.05  $\text{cc}/\text{m}^2\text{-day-atm}$ , and optimally 0.02  $\text{cc}/\text{m}^2\text{-day-atm}$ .

[0064] [EFFECTS OF THE INVENTION]

The present invention can give a composition with good

dispersion comprising EVOH and an inorganic layered compound. Molding this composition can give a film or a sheet with excellent gas barrier property. As a laminate, the present invention not only has excellent oxygen barrier property, but also very excellent barrier property against, for example, other gas molecules such as helium or nitrogen, carbonic acid gas, water, and low molecular weight fragrance ingredients such as limonene or menthol.

[0065] [WORKING EXAMPLES]

Next, the present invention will be discussed in detail by working examples, but is not to be taken as limited to these working examples.

[0066] **Working Example 1**

A montmorillonite aqueous dispersion of about 1 wt% concentration was prepared by the method of throwing 1 part by weight of high purity montmorillonite (trade name Kunipia G, made by Kunimine Industries Co., Ltd.) as an inorganic layered compound into 100 parts by weight of water while stirring, and dispersing by stirring until a uniform solution was formed. This dispersion was gradually combined with 350 parts by weight of 2-propanol and 25 parts by weight of 1-butanol while stirring vigorously to form a dispersion with a ratio by weight of dispersing solvents water/2-propanol/1-butanol = 2/7.5/0.5. This was called Solution A.

[0067] Five parts of EP-F101 (EVOH with ethylene copolymerization rate: 32% made by Kuraray Co., Ltd.; hereafter

abbreviated as EVOH-F) were thrown into 95 parts of solvent mixed at a ratio by weight of water/2-propanol = 3/7 and dissolved by heating to about 80°C and stirring for four hours to give a 5 wt% EVOH-F solution. This was called Solution B. Next, 56 parts of Solution A and 694 parts of Solution B were mixed to give 750 parts of a Solution C. Solution C had a ratio by weight of water/2-propanol/1-butanol solvent of water/2-propanol/1-butanol = 21/74/5, and a solid parts concentration of 0.56 wt% found by calculating.

[0068] This Solution C was passed through a high-pressure dispersion apparatus (trade name: Ultrahigh Pressure Homogenizer M110-E/H, made by Microfluidics Corporation) to give a uniform dispersion with good dispersion by one treatment at 1750 kgf/cm<sup>2</sup>. This was called Solution D. The particle size of the inorganic layered compound in this Solution D was 0.440 µm when measured in the same solvent.

[0069] **Working Example 2**

The Solution D prepared in Working Example 1 was coated and dried on a 12-µm thick biaxially drawn polyethylene terephthalate film (with corona-treated inner surface, trade name: Espot T4102, made by Toyo Boseki Kabushiki Kaisha) as a substrate to a thickness when dry of 0.05 µm using a Micro Gravure coater at a line speed of 6 m/min and a drying temperature of 100°C to give a laminate. Dry-laminating an undrawn LLDPE film (with corona-treated inner surface, trade name: TUS-FCS #40, made by Tohcello Co., Ltd.) onto the



resulting laminate using a commercial adhesive gave a laminate with good transparency when observed visually.

[BRIEF EXPLANATION OF THE DRAWINGS]

FIG. 1 is a schematic diagram showing the internal configuration of a high-pressure dispersion apparatus, and a setup for finely dispersing particles using a high-pressure high-shearing treatment.

FIG. 2 is a schematic graph showing the relation between the x-ray diffraction peak of an inorganic layered compound and the "unit thickness  $a$ " of this compound.

FIG. 3 is a schematic graph showing the relation between the x-ray diffraction peak of a resin composition containing an inorganic layered compound and the "spacing  $d$ " of this composition.

FIG. 4 is a schematic graph showing the relation between the x-ray diffraction peak of a resin composition and the "spacing  $d$ " of this composition when the peaks corresponding to the "spacing  $d$ " overlap a halo (or background), making the peak difficult to detect.

[EXPLANATION OF REFERENCE NUMBERS]

A: Sample charge

B: Pump pressure

C: Channel branch

D: Collision and shearing

E: Release of pressure and end of treatment

FIG. 1

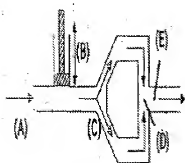
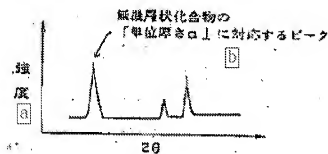
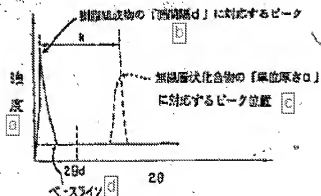


FIG. 2



Key: a) Intensity; b) Peak corresponding to "unit thickness a" of an inorganic layered compound.

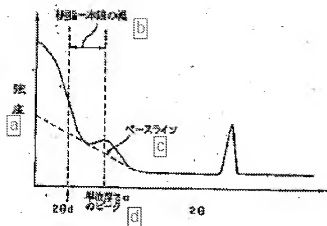
FIG. 3



$k$  = At least the width of one resin calculated by length  
 $\theta d$  → Diffraction angle corresponding to "unit thickness a + width of resin"

Key: a) Intensity; b) Peak corresponding to "spacing d" of a resin composition; c) Peak corresponding to "unit thickness a" of an inorganic layered compound; d) Baseline

FIG. 4



Key: a) Intensity; b) Width of one resin main chain; c) Baseline; d) Peak of unit thickness a